AD-A039 518   AEROSPACE CORP EL SEGUNDO CALIF CHEMISTRY AND PHYSICS LAB   F/G 7/4
                ABSORPTION AND DESORPTION RATES OF H2 AND D2 FOR LANI5, LACO5, --ETC(U)
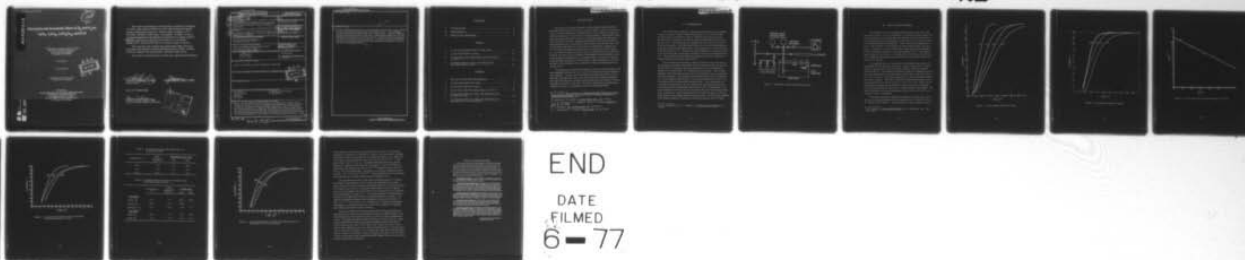   APR 77   C P MEILLEUR, M R MARTINELLI   F04701-76-C-0077
UNCLASSIFIED   TR-0077(2270-10)-2   SAMSO-TR-77-80   NL

| OF |
AD
A039 518

END
DATE
FILMED
6—77

ADA039518

Absorption and Desorption Rates of H_2 and D_2 for $LaNi_5$, $LaCo_5$, $LaNi_2Co_3$, and FeTi

Chemistry and Physics Laboratory
The Ivan A. Getting Laboratories
The Aerospace Corporation
El Segundo, Calif. 90245

19 April 1977

Interim Report

DDC

MAY 17 1977

C

AD No.
DDC FILE COPY

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract F04701-76-C-0077 with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P. O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by S. Siegel, Director, Chemistry and Physics Laboratory. Lieutenant A. G. Fernandez, SAMSO/YAPT, was the project officer for Advanced Space Programs.

This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Arturo G. Fernandez, Lt, USAF
Project Officer

Joseph Gassmann, Major, USAF

FOR THE COMMANDER

Floyd R. Stuart, Colonel, USAF
Deputy for Advanced Space Programs

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAMSO-TR-77-80	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ABSORPTION AND DESORPTION RATES OF H$_2$ AND D$_2$ FOR LaNi$_5$, LaCo$_5$, LaNi$_2$Co$_3$, AND FeTi		5. TYPE OF REPORT & PERIOD COVERED Interim rept.
		6. PERFORMING ORG. REPORT NUMBER TR-0077(2270-10)-2
7. AUTHOR(s) Christopher P. Meilleur, Michael R. Martinelli, and Stanley W. Mayer		8. CONTRACT OR GRANT NUMBER(s) F04701-76-C-0077
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Space and Missile Systems Organization Air Force Systems Command Los Angeles, Calif. 90009		12. REPORT DATE 19 April 1977
		13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Deuterium   Lanthanum Peritauichel
Iron Titanium   Ni-H$_2$ Battery
Hydrides
Hydrogen

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Rates of H$_2$ absorption and desorption were measured for LaNi$_5$, LaCo$_5$, LaNi$_2$Co$_3$, and FeTi in order to examine the limitations of these alloys for storing H$_2$ in high-power Ni-H$_2$ satellite batteries. If the H$_2$ absorption and desorption rates are sufficient, H$_2$ storage in the alloys could increase the energy density and decrease the volume of Ni-H$_2$ spacecraft batteries. The rate measurements showed that the quantity of H$_2$ absorbed or desorbed was linearly dependent on the square root of time for all four alloys. This

DD FORM 1473
(FACSIMILE)

409383

19. KEY WORDS (Continued)

PLUS OR MINUS

20. ABSTRACT (Continued)

rate law indicated that the rate-controlling step was hydrogen atom diffusion through an adherent hydride layer to the alloy surface. The activation energy for desorption from $LaNi_5$ was 4.5 ± 0.5 kcal. Even at $0.4°C$, the H_2 absorption and desorption rates were sufficient that batteries could be charged and discharged in less than 30 min. Rates for D_2 were also determined and found to be lower than for H_2. The use of $LaCo_5$ and $LaNi_2Co_5$ permitted even lower pressures than those needed with $LaNi_5$ for H_2 storage in $Ni-H_2$ satellite batteries.

CONTENTS

TABLES

FIGURES

I. INTRODUCTION

Because Ni-H$_2$ storage batteries can have higher energy densities[1] and longer lifetimes than the Ni-Cd and Ag-Zn batteries now used in space-craft, it would be desirable to eliminate most of the problems encountered with Ni-H$_2$ batteries: H$_2$ pressures as high as 500 psi, which demand heavy cell walls; large volume for storing H$_2$; and rather rapid self discharge.[2] It was shown by van Vucht, Kuijpers, and Bruning[3] that LaNi$_5$ can absorb large quantities of H$_2$ at pressures below 65 psi, where the cell walls need not be heavier than those for Ni-Cd cells, self discharge is slower, and 1 cm^3 of LaNi$_5$ hydride holds about twice as much H$_2$ as 1 cm^3 of liquid H$_2$. For the use of LaNi$_5$ storage of H$_2$ to be practical for Ni-H$_2$ batteries, however, the rates of H$_2$ desorption and absorption should be rapid enough to permit battery discharging and charging within a 1 hr period. Because of the practical importance of these kinetics, measurements were made of the rates of H$_2$ absorption and desorption by LaNi$_5$ at temperatures from zero to 32°C.

It was shown by Kuijpers[4] that hydrides of LaCo$_5$ and LaCo$_3$Ni$_2$ reach their equilibrium pressures at even lower pressures than those required to form LaNi$_5$H$_6$. Because this would allow even lower pressures in Ni-H$_2$ batteries, H$_2$ absorption rates were also measured for these two alloys. Because FeTi alloy also absorbs large amounts of H$_2$ as FeTiH$_2$,[5] FeTiH$_2$ desorption rates were measured. In order to enhance our understanding of these new alloys, D$_2$ absorption rates were also determined.

[1] R. W. Easter, Proceedings of the Ninth Intersociety Energy Conversion Engineering Conference, American Society of Mechanical Engineers, New York (1974), pp. 888-895.

[2] J. Giner and J. D. Dunlop, J. Electrochem. Soc. 122, 4 (1975).

[3] J. H. N. van Vucht, F. A. Kuijpers, and H. C. Bruning, Philips Res. Rep. 25, 133 (1970).

[4] F. A. Kuijpers, Ber. Bunsen Gesel. 76, 1220 (1972).

[5] J. J. Reilly and R. H. Wiswall, Inorg. Chem. 13, 218 (1974).

II. EXPERIMENTAL

The LaNi$_5$ (Ronson Metals Corporation purified grade) was activated by using a process similar to that used by Kuijpers.[4] 9.94 g of freshly crushed LaNi$_5$ was placed in a 300 cm^3 stainless steel pressure bomb, the vessel was evacuated, and then the alloy was exposed to 40 atm hydrogen for 18 hr. This procedure was repeated two times before the activation was successful. After this first activation, the bomb was transferred to the rate measurement system (Fig. 1) and immersed in a water bath controlled to within ±0.1°C. The alloy was then subjected to a cycling sequence of 20 successive steps of hydrogen absorption followed by hydrogen desorption. This cycling sequence decreased the particle size and resulted in a constant surface area for the alloy powder.[6]

The absorption and desorption rates of hydrogen were measured by monitoring the variation of hydrogen pressure above the alloy as a function of time with a Uni-measure pressure transducer that was connected to a Moseley x-t recorder (Fig. 1). Duplicate runs were made. The average deviation of the pressure from the mean of the duplicate runs was typically less than 6 percent. The hydrogen used for absorption runs was contained in a 1-liter stainless steel vessel. For measuring absorption, this vessel was opened to the evacuated alloy-sample vessel. After absorption was completed, the desorption rate was measured by permitting the hydrogen to desorb from the hydrided alloy into several 1-liter vacuum flasks. The same procedures were also used in measuring the absorption and desorption rates of deuterium. Rate measurements were made for LaCo$_5$, LaNi$_2$Co$_3$ (both donated by the Philips Research Laboratories), and FeTi alloy (donated by Brookhaven National Laboratory) with the procedures used for LaNi$_5$.

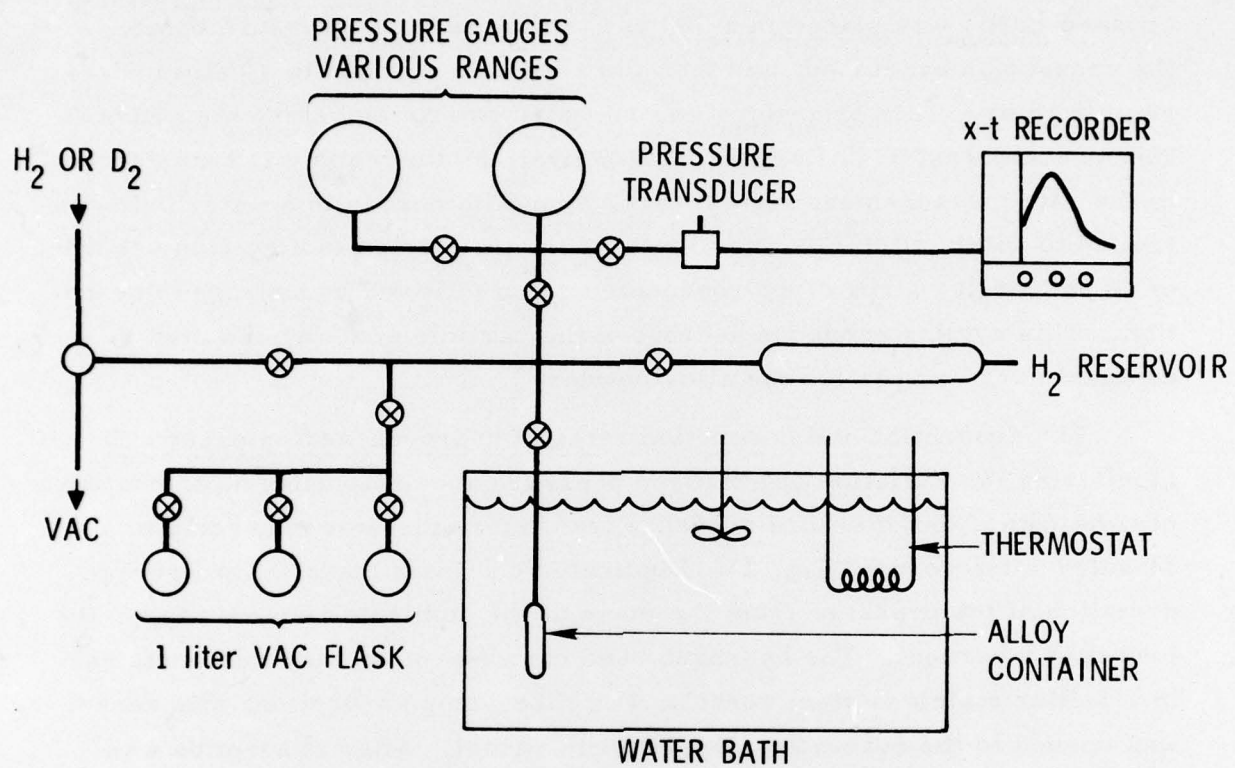[6]H. H. van Mal and K. H. J. Buschow, <u>J. Less-Common Metals</u> <u>35</u>, 65 (1974).

Figure 1. Schematic of Rate Measuring Apparatus

III. RESULTS AND DISCUSSION

The results for the H_2 desorption and absorption rates with $LaNi_5$ are shown in Figs. 2 and 3, respectively. The abscissa is the square root of time because it was consistently noted that the amount of H_2 desorbed and absorbed had a linear dependence on the square root of time up to about 60 percent desorption and absorption. Such a square-root dependence on time is not uncommon for the reaction of alloys with hydrogen[7] and other gases. It is known to occur when the rate-controlling step is diffusion of H-atoms through an adherent, crack-free hydride layer.[7] If the hydride layer, however, has cracks or is nonadherent, the amount of H_2 absorbed or desorbed will be proportional to the time of contact rather than to the square root of time.

It is apparent in Fig. 2 that the rate of desorption decreased as the temperature of the alloy was decreased. Figure 4 shows the T^{-1} dependence for the log of the slope of the linear section of the H_2 desorption curves in Fig. 2. The activation energy for diffusion of hydrogen atoms in the $LaNi_5$ hydride layer was calculated from the slope of the line in Fig. 4 to be 4.5 ± 0.5 kcal. The times required for 95 and 98 percent desorption are given in Table 1. The time required for 98 percent desorption of the H_2 decreased from 25 min at 0.4°C to 2.6 min at 32.0°C. These desorption times are sufficiently rapid that it would be practical to discharge Ni-H_2 batteries within 30 min if such a rapid discharge were needed. The times required for 95 percent desorption of H_2 at 0.4° and 32.0°C were 16 and 2.2 min, respectively.

The times required for 98 percent absorption by $LaNi_5$ (Fig. 3) of the H_2 at an initial pressure of 140 psi ranged from 4.5 min at 22.0°C to 1.7 min at 0.4°C (Table 2). These times are short enough to permit

---

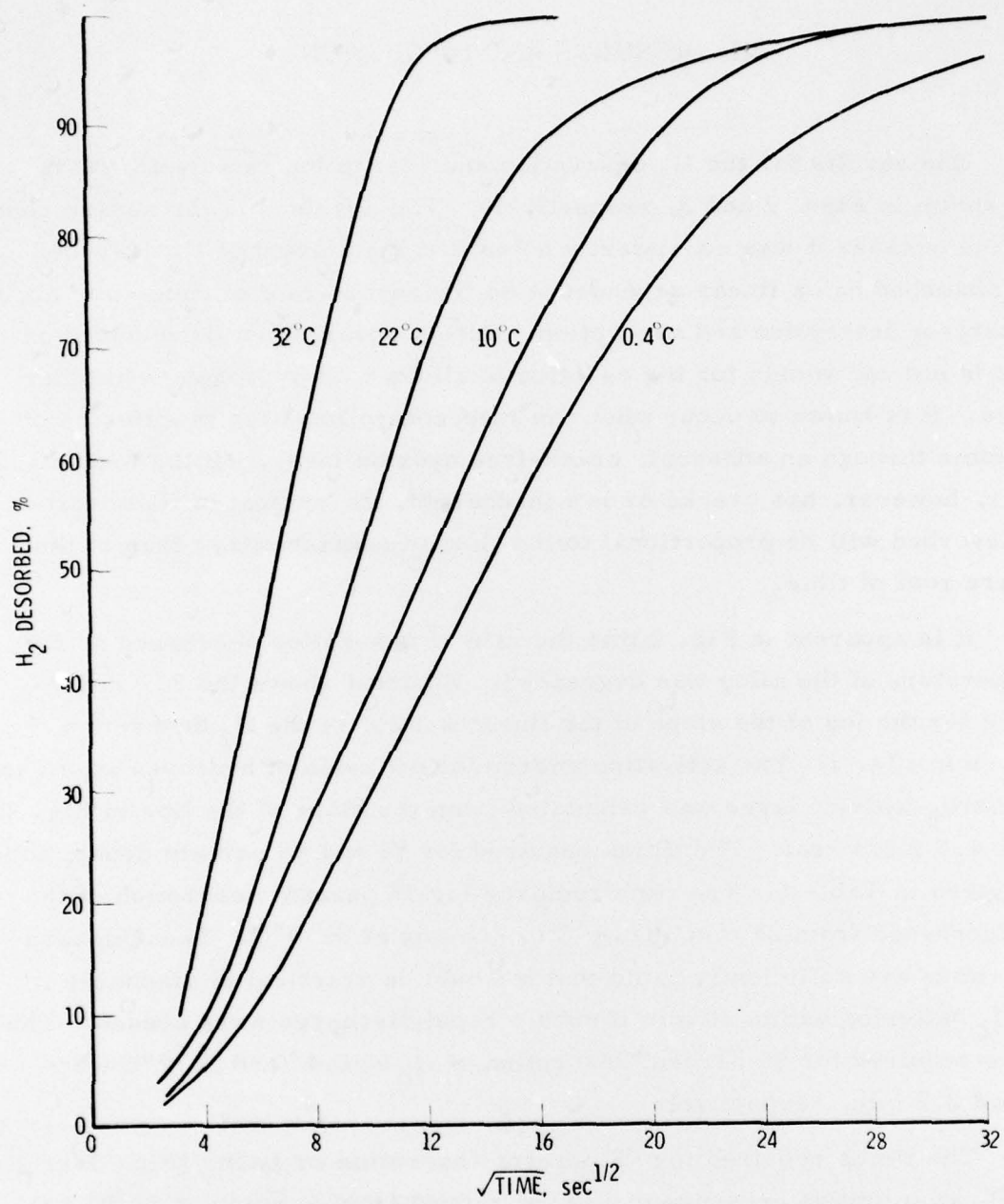[7] G. G. Libowitz, Binary Metal Hydrides, W. A. Benjamin, Inc., New York (1965).
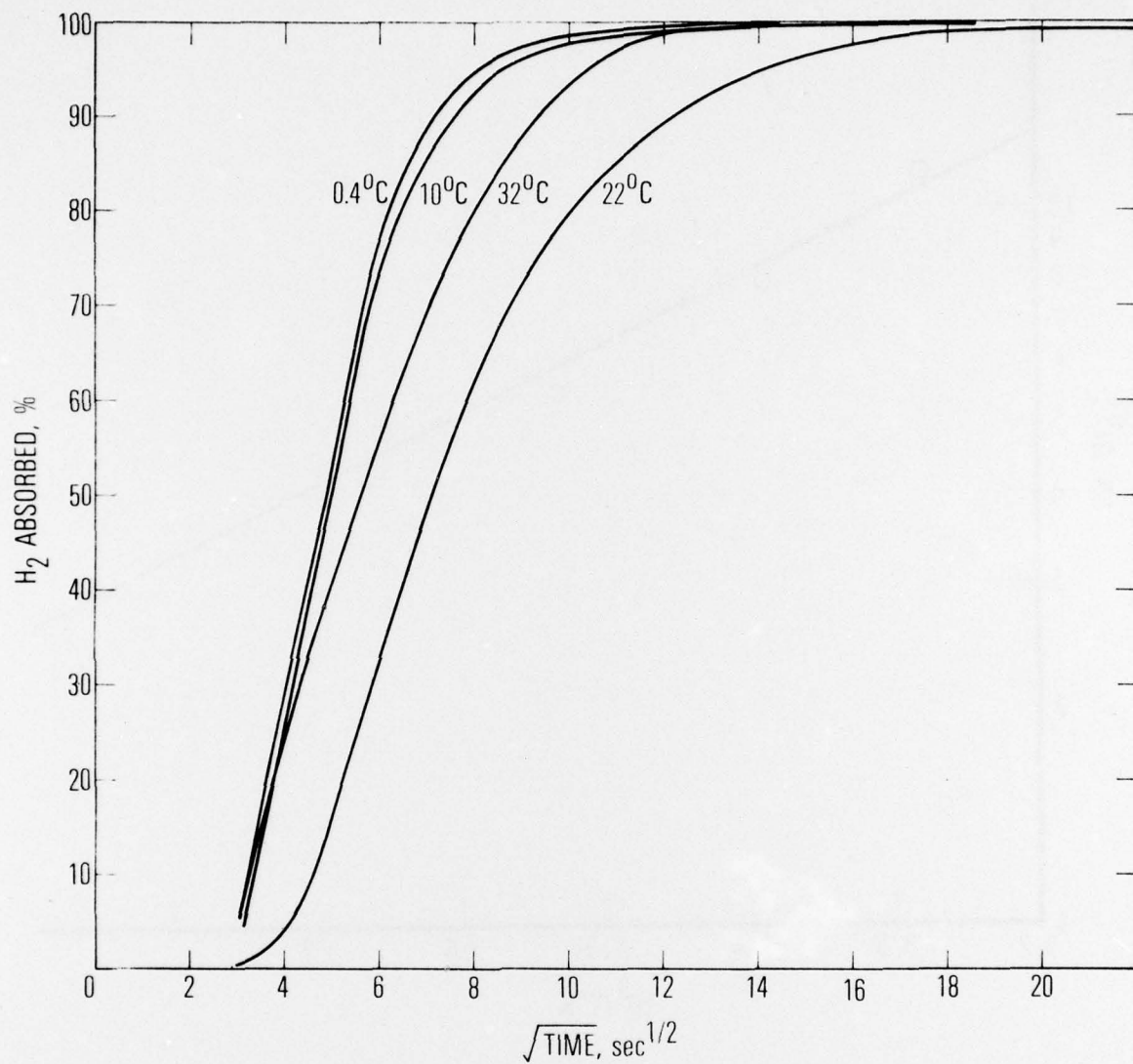
-7-

Figure 2. H_2 Desorption Rates from $LaNi_5$
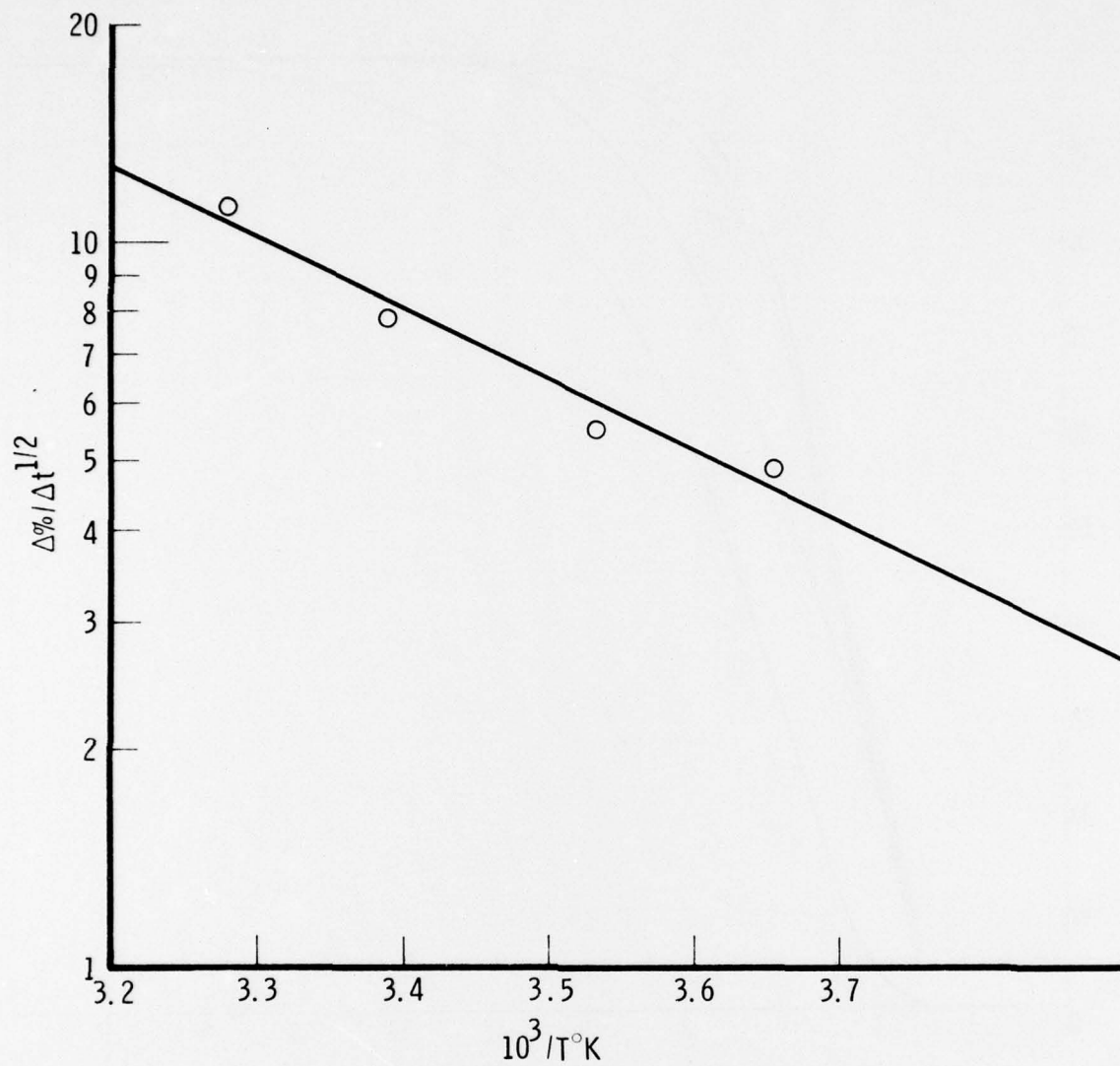
Figure 3. H_2 Absorption Rates for $LaNi_5$

-9-

20

10
9
8
7

6

$\Delta\%/\Delta t^{1/2}$ 5

4

3

2

1
3.2   3.3   3.4   3.5   3.6   3.7

$10^3/T°K$

Figure 4.   Log of LaNi$_5$ Alloy Desorption Rates vs $10^3/T°K$

-10-

Table 1. H_2 and D_2 Desorption Rates for $LaNi_5$ Alloy

| Temperature, °C | Slope $(\Delta\%/\Delta t^{1/2})$, $sec^{-1/2}$ | Desorption Time, min | | Deuterium Slope $(\Delta\%/\Delta t^{1/2})$, $sec^{-1/2}$ |
		95%	98%	
32.0	11.4	2.2	2.6	11.1
22.0	7.9	7.0	10.4	7.5
10.0	5.6	8.8	11.7	
0.4	4.9	15.7	24.8	

Table 2. H_2 Absorption Rates for $LaNi_5$, with Initial
Reservoir Pressure of 140 psi

| Temperature, °C | Slope, $sec^{-1/2}$ | Absorption Time, min | |
		95%	98%
32.0	15.5[a]	1.9	2.2
22.0	16.7	3.3	4.5
10.0	24.0	1.3	1.9
0.4	24.0	1.2	1.7

[a]The slope for D_2 absorption was 9.0 at 32.0°C.

convenient absorption by LaNi$_5$ of H$_2$ generated during the charging of Ni-H$_2$ batteries. The linear portion of each absorption curve in Fig. 3 does not extend to much above 60 percent H$_2$ absorbed. This nonlinearity is expected to arise because, as the hydride layer becomes thicker, the surface area of the unreacted LaNi$_5$ becomes smaller. The rate of absorption depends on the LaNi$_5$ surface area, which decreases because the alloy is replaced by the hydride layer.

Inasmuch as the Ni-H$_2$ cell wall thickness required to withstand the H$_2$ pressure would be even less at an initial H$_2$ pressure of 70 psi than at the 140 psi of Fig. 3, absorption rate measurements were made with an initial pressure of 70 psi for three temperatures (Fig. 5). The times required for 98 percent absorption by LaNi$_5$ at 10.0 to 32.0°C are shown in Table 3. The increase in absorption times and decrease in slope with increased temperature can be attributed to the increase of the equilibrium pressure of the hydride at the higher temperatures.[3] In this case the faster diffusion rates at the higher temperatures are not sufficient to outweigh the effect of the increase in equilibrium pressure. Nevertheless, the absorption times are short enough to permit discharge of the Ni-H$_2$ battery in less than 30 min.

In Fig. 6, the absorption rates at 22.0°C are compared for initial H$_2$ pressures of 50, 70, and 140 psi. Even at an initial pressure of 50 psi, the rate of H$_2$ absorption by LaNi$_5$ was high enough to permit 98 percent discharge of a Ni-H$_2$ battery in about the same time required as with initial H$_2$ pressure of 70 psi.

Because the transition equilibrium pressures for LaCo$_5$ and LaNi$_2$Co$_3$[4] are considerably lower than for LaNi$_5$, lower H$_2$ pressures could be used in the Ni-H$_2$ cells than are required for LaNi$_5$ storage of H$_2$. In Table 4, data are given for the absorption times and slopes for these cobalt-containing alloys at initial H$_2$ pressures of 30 psi. Only 7.3 min were required for 98 percent absorption of H$_2$ on LaNi$_2$Co$_3$ at 25.7°C. For LaCo$_5$, 40 min
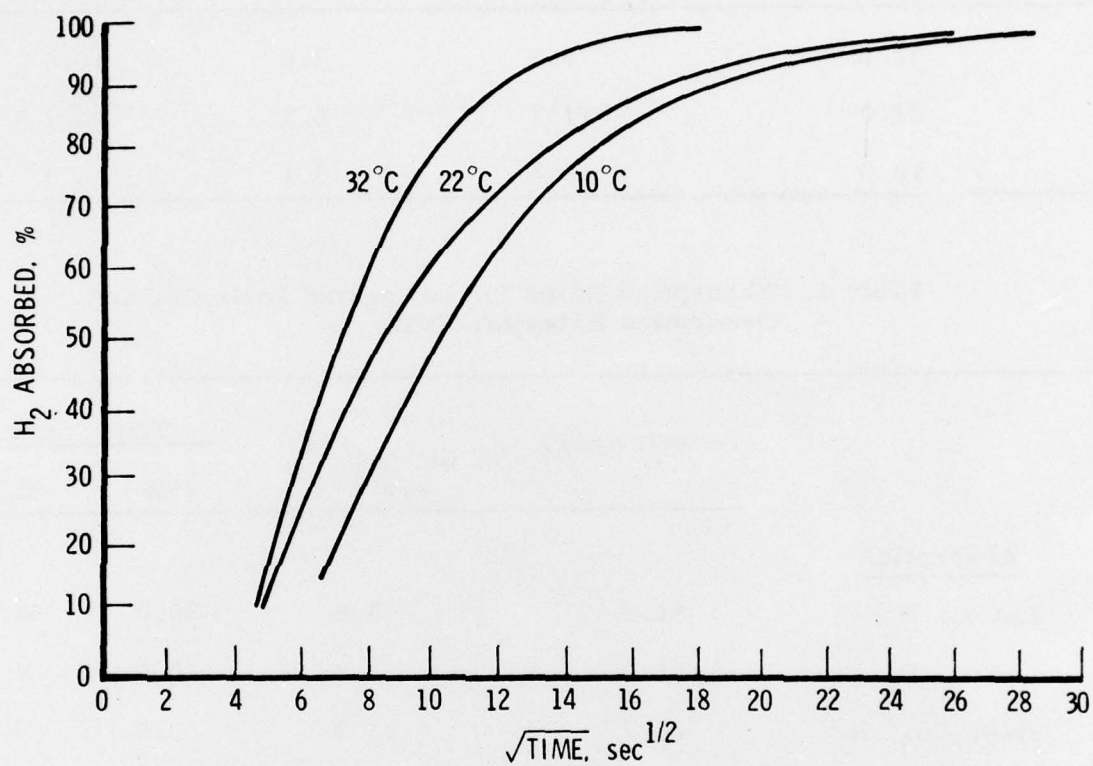
-12-

Figure 5. H_2 Absorption Rates for $LaNi_5$ with Initial
Reservoir Pressure of 70 psi

Table 3. H_2 Absorption Rates with Initial Reservoir Pressure of 70 psi

Temperature, °C	Slope $(\Delta\%/\Delta t^{1/2})$, $sec^{-1/2}$	Absorption Time, min	
		95%	98%
32.0	9.9	7.6	10.9
22.0	11.1	6.7	9.1
10.0	15.4	3.1	.4.1

Table 4. Absorption Rates for $LaCo_5$ and $LaNi_2Co_3$ and Desorption Rates for FeTi

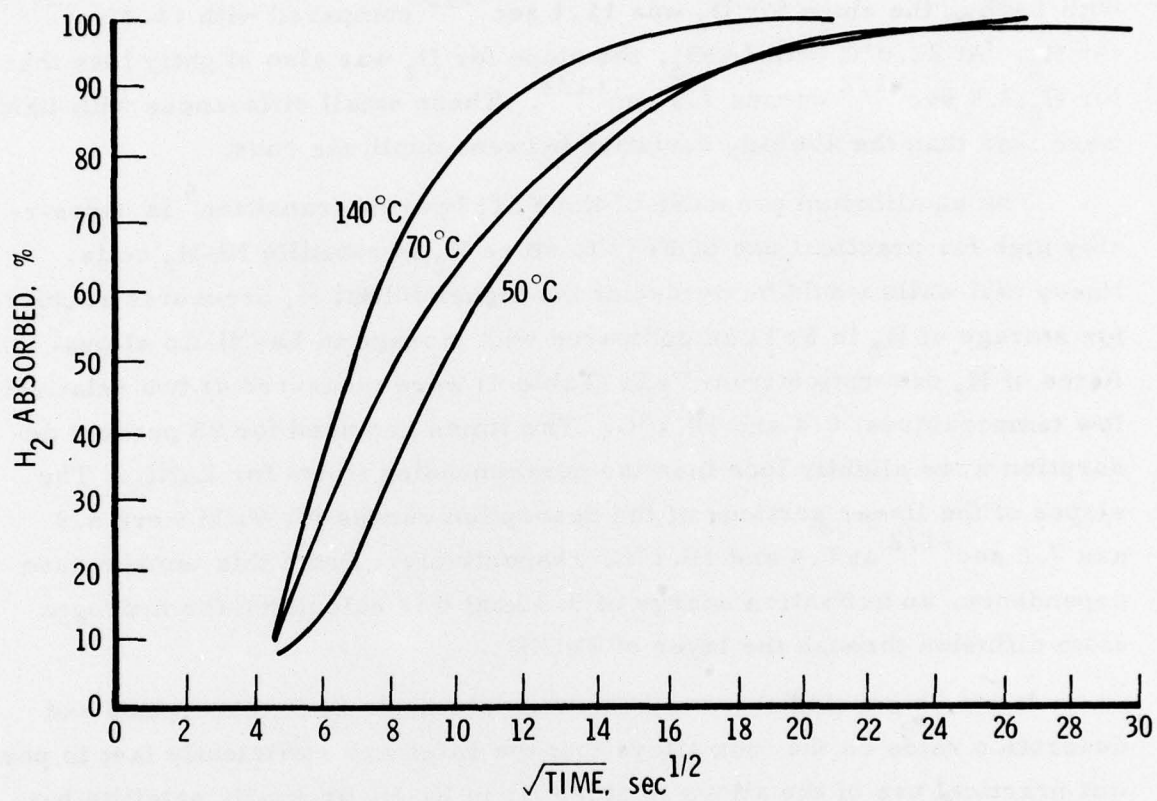|	Temperature, °C	Slope $(\Delta\%/\Delta t^{1/2})$, $sec^{-1/2}$	Time, min	
			95%	98%
Absorption				
$LaCo_5$, H_2	51.0	3.8	20.0	40.0
$LaCo_5$, D_2	51.0	3.2	40.0	-
$LaNi_2Co_3$, H_2	25.7	13.3	3.8	7.3
Desorption				
FeTi, N_2	10.1	7.2	6.8	10.4
FeTi, H_2	0.4	5.9	13.1	22.1

Figure 6. H_2 Absorption Rates for LaNi$_5$ with Initial Reservoir
Pressures of 50, 70, and 140 psi

were required for 98 percent H_2 absorption and 20 min for 95 percent H_2 absorption. Deuterium is absorbed on $LaCo_5$ more slowly than hydrogen (Table 4); 40 min were required for 95 percent absorption of D_2. The slope of the linear portion of the absorption curve for D_2 was 3.2 $sec^{-1/2}$ compared with 3.8 $sec^{-1/2}$ for H_2. A smaller difference between D_2 and H_2 kinetics was observed with $LaNi_5$ than with $LaCo_5$. At 32.0°C (Table 1) with $LaNi_5$, the slope for D_2 was 11.1 $sec^{-1/2}$ compared with 11.4 $sec^{-1/2}$ for H_2. At 22.0°C with $LaNi_5$, the slope for D_2 was also slightly less than for H_2: 7.5 $sec^{-1/2}$ versus 7.9 $sec^{-1/2}$. These small differences with $LaNi_5$ were less than the average deviation between duplicate runs.

The equilibrium pressure of the FeTi hydride transition[5] is undesirably high for practical use of FeTi to store H_2 in satellite $Ni-H_2$ cells. Heavy cell walls would be needed at the higher initial H_2 pressures required for storage of H_2 in FeTi as compared with storage in La-Ni-Co alloys. Rates of H_2 desorption from FeTi (Table 4) were measured at two relatively low temperatures; 0.4 and 10.1°C. The times required for 98 percent desorption were slightly less than the corresponding times for $LaNi_5$. The slopes of the linear portions of the desorption curves for FeTi were 5.9 and 7.2 $sec^{-1/2}$ at 0.4 and 10.1°C, respectively. From this temperature dependence, an activation energy of 3.3 kcal was calculated for hydrogen atom diffusion through the layer of $FeTiH_2$.

It can be concluded from these measurements of H_2 absorption and desorption rates on the four alloys that the rates are sufficiently fast to permit practical use of the alloys to store H_2 in $Ni-H_2$ or $Ag-H_2$ satellite batteries. The relatively high transition pressures for FeTi, however, make it less desirable than $LaNi_5$ in providing a weight savings by the use of lighter walls for the cells. On the other hand, $LaNi_5$ may be less advantageous than $LaNi_2Co_3$ because its higher transition pressures would require the use of heavier cell walls. It is recommended, therefore, that investigation be carried out to compare $LaNi_5$, $LaNi_2Co_3$, and other La-Ni-Co alloys in order to determine which would provide the highest battery energy density and the longest battery lifetimes.

THE IVAN A. GETTING LABORATORIES

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military concepts and systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space and missile systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch and reentry aerodynamics, heat transfer, reentry physics, chemical kinetics, structural mechanics, flight dynamics, atmospheric pollution, and high-power gas lasers.

Chemistry and Physics Laboratory: Atmospheric reactions and atmospheric optics, chemical reactions in polluted atmospheres, chemical reactions of excited species in rocket plumes, chemical thermodynamics, plasma and laser-induced reactions, laser chemistry, propulsion chemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, photosensitive materials and sensors, high precision laser ranging, and the application of physics and chemistry to problems of law enforcement and biomedicine.

Electronics Research Laboratory: Electromagnetic theory, devices, and propagation phenomena, including plasma electromagnetics; quantum electronics, lasers, and electro-optics; communication sciences, applied electronics, semiconducting, superconducting, and crystal device physics, optical and acoustical imaging; atmospheric pollution; millimeter wave and far-infrared technology.

Materials Sciences Laboratory: Development of new materials; metal matrix composites and new forms of carbon; test and evaluation of graphite and ceramics in reentry; spacecraft materials and electronic components in nuclear weapons environment; application of fracture mechanics to stress corrosion and fatigue-induced fractures in structural metals.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, studies of solar magnetic fields; space astronomy, x-ray astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.

THE AEROSPACE CORPORATION
El Segundo, California